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# Tight-Binding Cluster Model for C, Si, and Ge

## I. Analytic Solution for s-States in Diamond Lattice

By

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Using the tight-binding approximation an analytic solution of the Schrödinger equation for the s-states of C, Si, and Ge clusters in the form of a rectangular parallelepiped is found and discussed.

Unter Benutzung der Tight-Binding-Approximation wird eine analytische Lösung der Schrödingergleichung für die s-Zustände quaderförmiger C-, Si- bzw. Ge-Cluster gefunden und diskutiert.

### 1. Introduction

The tight-binding method in the nearest- or next-nearest-neighbour approximation for the infinite diamond (C, Si, Ge) or zincblende crystals (GaAs, ZnSe) provides a very good description of their valence bands [1]. The importance of the description of the electronic structure of the infinite crystals in question (C, Si, Ge) is obvious. From the point of view of applications, however, the investigation of finite clusters or thin films having a surface is even more important.

It follows from the calculations on the infinite crystals [1] that the hybridization of the s- and p-states is in general necessary. It appears, however, that the inclusion of the s-states only provides a very good description of the lowest part of the valence band of these crystals to within a few tenths of an eV accuracy throughout the Brillouin zone. Therefore, we use in the first approximation the s-functions only. Together with other assumptions discussed later, this leads to a very important advantage — we are able to solve the Schrödinger equation analytically.

The clusters investigated in this work have a very simple geometrical form — we consider clusters in the form of a rectangular parallelepiped. In general, the relaxation of the surface (the change of the lattice constant near the surface, other values of the tight-binding parameters in this region, etc.) is to be expected. Within the tight-binding method, one must take the necessary modifications from the experiment or results of more sophisticated methods. As the modified parameters for the surface are not known, we do not consider any relaxation in the surface region here. We assume the same tight-binding parameters both inside the cluster and near its surface. The only difference with respect to the infinite crystal is the existence of the surface where the corresponding boundary conditions must be fulfilled. In principle, our analytic solution can be used as the starting point for the inclusion of the surface relaxation, for example, by the resolvent technique (the Dyson equation). In this case, however, the inclusion of the p-states is obviously necessary.

The advantage of the analytic solution of the Schrödinger equation is obvious. One can easily compare the electronic states of the infinite crystal and the cluster and investigate the convergence of the cluster properties to their bulk limit. From this

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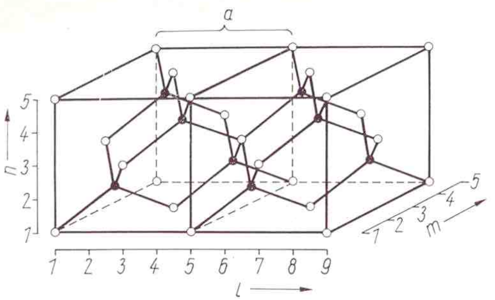

Fig. 1. The diamond lattice consists of two f.c.c. sublattices (○ and ●). The lattice constant is equal to $a$. For the cluster shown here, $L = 9$ and $M = N = 5$

point of view, this paper represents a further one in a series of works on the analytic cluster model with the s.c., f.c.c., and b.c.c. lattices [2 to 7]. We mention here a few results. The analytic cluster model enables to define for the finite clusters the Brillouin zone with discrete $\boldsymbol{k}$-vectors in analogy with the infinite crystal theory. The analytic formulae for the band width, binding energy, etc., enable to find analytic, asymptotically valid formulae for the convergence of these properties to their bulk limits and thus to estimate the rate of their convergence. The physical meaning of the periodical Born-Kármán conditions has been further clarified by this model [5]. The successful application of the asymptotical formulae for the binding energy, band width, and the lower band edge to the results of the CNDO calculations on the lithium clusters [8] shows the usefulness of this approach. The significance of these results for the theory of the cluster properties is obvious.

The diamond lattice has two atoms per elementary cell. This leads to a more complicated structure of the tight-binding Hamiltonian and to a more complicated form of the solution of the corresponding Schrödinger equation. For this reason, we present our results in two parts. In this part (I), we describe the form of the clusters, the corresponding Hamiltonian, and solve the Schrödinger equation. In Part II, the results presented in I are used for the investigation of the convergence of some electronic properties of the clusters to their bulk limit. Some results of this work were reported in [9].

## 2. Description of Clusters

We consider clusters with the diamond lattice in the form of rectangular parallelepipeds (see Fig. 1). The diamond lattice consists of two f.c.c. sublattices (atoms ○ and ● in Fig. 1). A simple description of the diamond lattice sites can be achieved by means of the s.c. lattice with the lattice constant $a/4$,

$$(lmn) = \boldsymbol{r}_{lmn} = (l\boldsymbol{i} + m\boldsymbol{j} + n\boldsymbol{k})\, a/4\,;$$
$$l = 1, \dots, L; \quad m = 1, \dots, M; \quad n = 1, \dots, N\,.$$

The atoms forming the sublattice ○ are at the sites for which all $l$, $m$, $n$ are odd and $l + m + n = 4k + 3$. The lattice sites ● are those for which all $l$, $m$, $n$ are even and $l + m + n = 4k + 2$. Here, $\boldsymbol{i}, \boldsymbol{j}$ and $\boldsymbol{k}$ are the unit vectors giving the Cartesian axes. $L$, $M$, and $N$ give the size and shape of the cluster. $k$ is an integer.

Since the diamond lattice consists of two sublattices, various forms of clusters having ○ or ● atoms on different faces of the parallelepiped can be considered. We consider here only the clusters having the same (say ○) atoms on the surface. All atoms ● lie inside the cluster. It means that we assume $L = 4\lambda + 1$, $M = 4\mu + 1$, and $N = 4\nu + 1$, where $\lambda$, $\mu$, and $\nu$ are integers. The number of atoms in the sublattices ○ and ● is then equal to $[1 + (2\lambda + 1)\,(2\mu + 1)\,(2\nu + 1)]/2$ and $4\lambda\mu\nu$, respectively.

## 3. Hamiltonian

The tight-binding electronic wave function $\psi(\boldsymbol{r})$ is a linear combination of the atomic orbitals located at the corresponding lattice sites. In agreement with the discussion in the Introduction, we use the s-states model, in which there is only one s-like atomic orbital $\varphi$ at each lattice site so that

$$\psi(\boldsymbol{r}) = \sum_{lmn}{}^{\circ}\, c^{\circ}_{lmn}\varphi(\boldsymbol{r} - \boldsymbol{r}_{lmn}) + \sum_{lmn}{}^{\bullet}\, c^{\bullet}_{lmn}\varphi(\boldsymbol{r} - \boldsymbol{r}_{lmn})\,. \tag{1}$$

Here, the sums $\sum^{\circ}$ and $\sum^{\bullet}$ run over the corresponding sublattices.

Using the wave function (1) we have to solve the matrix eigenvalue problem

$$H\boldsymbol{c} = E\boldsymbol{c}\,. \tag{2}$$

Here, $\boldsymbol{c}$ is a column vector with the components $c^{\circ}_{lmn}$ and $c^{\bullet}_{lmn}$. The matrix $H$ has in the nearest-neighbour approximation the form

$$H_{lmn,lmn} = \alpha\,,$$

$$H_{lmn,l'm'n'} = \begin{cases} \beta & \text{if atoms } (lmn) \text{ and } (l'm'n') \text{ are nearest neighbours,} \\ 0 & \text{otherwise.} \end{cases}$$

For C, Si, and Ge, the atoms ○ and ● are of the same kind. The parameter $\alpha$ determines the zero of energy and can be put equal to zero. The values of the tight-binding parameter $V_{\mathrm{ss}}$ obtained for the infinite crystal [1] are related to our $\beta$-parameter by $\beta = V_{\mathrm{ss}}/4$.

Now, in order to better understand the structure of the eigenvalue problem (2), we rewrite it as an equivalent system of two coupled difference equations,

$$(\alpha - E)\, c^{\bullet}_{lmn} + \beta(c^{\circ}_{l-1,m-1,n-1} + c^{\circ}_{l-1,m+1,n+1}, + c^{\circ}_{l+1,m-1,n+1} + $$
$$+ c^{\circ}_{l+1,m+1,n-1}) = 0 \tag{3a}$$

and

$$(\alpha - E)\, c^{\circ}_{lmn} + \beta(c^{\bullet}_{l+1,m+1,n+1} + c^{\bullet}_{l+1,m-1,n-1} + c^{\bullet}_{l-1,m+1,n-1} + $$
$$+ c^{\bullet}_{l-1,m-1,n+1}) = 0\,, \tag{3b}$$

together with the corresponding surface boundary conditions which are not given explicitly here. According to (3a), each atom ● interacts with four neighbouring atoms ○ lying at the corners of the tetrahedron. Similarly, each atom ○ not lying at the surface of the cluster interacts with four atoms ● (equation (3b)). For atoms at the surface, however, some neighbours ● are missing. Instead of writing down the corresponding modifications of (3b) for different surface lattice sites and solving the resulting complicated system of equations we use a much more elegant way.

An equivalent way is to extend the validity of (3b) to all atoms ○ in the cluster and require at the same time that all coefficients $c^{\bullet}_{lmn}$ referring to the non-existing neighbours ● are equal to zero,

$$c^{\bullet}_{0,m,n} = c^{\bullet}_{L+1,m,n} = c^{\bullet}_{l,0,n} = c^{\bullet}_{l,M+1,n} = c^{\bullet}_{l,m,0} = c^{\bullet}_{l,m,N+1} = 0\,. \tag{4}$$

A more detailed discussion of the boundary conditions of this form can be found in [5].

## 4. Energies and Wave Function for $E \neq \alpha$

In the case $E \neq \alpha$, difference equations (3) can be solved by eliminating the coefficient $c^{\circ}_{lmn}$. Calculating $c^{\circ}_{lmn}$ from (3b) and substituting it into (3a) we get the equation for the atoms ● only,

$$[(E-\alpha)^2 - 4\beta^2]\, c^{\bullet}_{l,m,n} - \beta^2 (c^{\bullet}_{l-2,m-2,n} + c^{\bullet}_{l-2,m+2,n} + c^{\bullet}_{l+2,m-2,n} + c^{\bullet}_{l+2,m+2,n} + c^{\bullet}_{l-2,m,n-2} + c^{\bullet}_{l-2,m,n+2} + c^{\bullet}_{l+2,m,n-2} + c^{\bullet}_{l+2,m,n+2} + c^{\bullet}_{l,m-2,n-2} + c^{\bullet}_{l,m-2,n+2} + c^{\bullet}_{l,m+2,n-2} + c^{\bullet}_{l,m+2,n+2}) = 0\,. \tag{5}$$

Boundary conditions (4) remain unchanged.

To solve this difference equation, we can make use of the results known from the calculations on the f.c.c. clusters [5]. The structure of the f.c.c. difference equation is exactly the same as that of (5) except for the substitutions $[(E-\alpha)^2 - 4\beta^2] \to E - \alpha$ and $\beta^2 \to \beta$. Therefore, using the known formula for the energies of the f.c.c. clusters [5] we get the energies of the diamond clusters in the form

$$E_{pqr\pm} = \alpha \pm 4\beta \left[\cos^2\left(\frac{a}{4}\, k^{pqr}_x\right) \cos^2\left(\frac{a}{4}\, k^{pqr}_y\right) \cos^2\left(\frac{a}{4}\, k^{pqr}_z\right) + \sin^2\left(\frac{a}{4}\, k^{pqr}_x\right) \sin^2\left(\frac{a}{4}\, k^{pqr}_y\right) \sin^2\left(\frac{a}{4}\, k^{pqr}_z\right)\right]^{1/2}. \tag{6}$$

Here, the definition of the discrete **k**-vector

$$\boldsymbol{k}^{pqr} = \left(\frac{4p\pi}{(L+1)\,a}, \frac{4q\pi}{(M+1)\,a}, \frac{4r\pi}{(N+1)\,a}\right), \tag{7}$$

is the same as in the case of the f.c.c. clusters [5] except for the different lattice constant $a$ used here. From all possible **k**-vectors corresponding to

$$p = 1, \ldots, \frac{L-1}{2}, \qquad q = 1, \ldots, \frac{M-1}{2}, \quad \text{and} \quad r = 1, \ldots, \frac{N-1}{2} \tag{8}$$

only those for which

$$k_x + k_y + k_z \leqq \frac{3\pi}{a} \tag{9}$$

give non-equivalent physical states. All $4\lambda\mu\nu$ states of the diamond cluster lie in the octant $k_x, k_y, k_z > 0$ of the Brillouin zone of the infinite f.c.c. crystal.

Energies (6) form two parts of the band which are symmetrical with respect to the central level $E = \alpha$. This symmetry results from the fact that the diamond lattice consists of two sublattices ○ and ●, the atoms of each of them do not mutually interact. Using quantum-chemical terminology our diamond cluster is an odd alternant. This has also further consequences which will not be discussed here [10].

To get eigenvectors for the diamond clusters we can again use the eigenvectors of the f.c.c. clusters. Having in mind the different lattice constant we get for the coefficients corresponding to the sublattice ● the following formula:

$$c^{\bullet pqr}_{lmn} = N^{pqr} \sin\left(\frac{a}{4}\, lk^{pqr}_x\right) \sin\left(\frac{a}{4}\, mk^{pqr}_y\right) \sin\left(\frac{a}{4}\, nk^{pqr}_z\right), \tag{10}$$

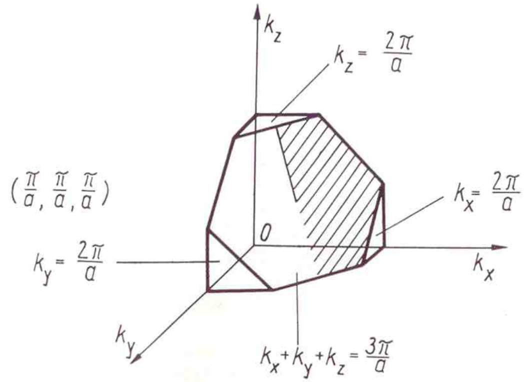

Fig. 2. The discrete wave vector $\boldsymbol{k}_{pqr}$ giving all states $E \neq \alpha$ of the diamond cluster lie in one eighth of the f.c.c. Brillouin zone. Two states correspond to each **k**-vector

where $N^{pqr}$ is a normalizing factor. The coefficients $c^{\circ pqr}_{lmn}$ can easily be calculated from (3b). We get

$$c^{\circ pqr\pm}_{lmn} = \mp N^{pqr} \left[\cos^2\left(\frac{a}{4}\, k^{pqr}_x\right) \cos^2\left(\frac{a}{4}\, k^{pqr}_y\right) \cos^2\left(\frac{a}{4}\, k^{pqr}_z\right) + \sin^2\left(\frac{a}{4}\, k^{pqr}_x\right) \sin^2\left(\frac{a}{4}\, k^{pqr}_y\right) \sin^2\left(\frac{a}{4}\, k^{pqr}_z\right)\right]^{-1/2} \times \left[\sin \frac{a}{4}\, lk^{pqr}_x\right) \sin\left(\frac{a}{4}\, mk^{pqr}_y\right) \sin\left(\frac{a}{4}\, nk^{pqr}_z\right) \times \cos\left(\frac{a}{4}\, k^{pqr}_x\right) \cos\left(\frac{a}{4}\, k^{pqr}_y\right) \cos\left(\frac{a}{4}\, k^{pqr}_z\right) + \cos\left(\frac{a}{4}\, lk^{pqr}_x\right) \cos\left(\frac{a}{4}\, mk^{pqr}_y\right) \cos\left(\frac{a}{4}\, nk^{pqr}_z\right) \times \sin\left(\frac{a}{4}\, k^{pqr}_x\right) \sin\left(\frac{a}{4}\, k^{pqr}_y\right) \sin\left(\frac{a}{4}\, k^{pqr}_z\right)\right]. \tag{11}$$

The normalizing factor $N^{pqr}$ equals

$$N^{pqr} = \left[\frac{64}{(L+1)\,(M+1)\,(N+1)}\right]^{1/2}.$$

Equations (6), (10), and (11) together with the definition of the discrete **k**-vector (7) to (9) give the analytic energies and wave functions in the case $E \neq \alpha$. In agreement with the fact that the diamond crystal has the f.c.c. structure with two atoms in the elementary cell, the wave vectors $\boldsymbol{k}^{pqr}$ lie in the first Brillouin zone of the f.c.c. crystal and two states correspond to each $\boldsymbol{k}^{pqr}$. Only one eighth of the zone in the octant $k_x, k_y, k_z > 0$ gives non-equivalent states in agreement with [5] (see Fig. 2).

## 5. Case $E = \alpha$

In the preceding section, we have found $8\,\lambda\mu\nu$ solutions for $E \neq \alpha$. The degeneracy of the level $E = \alpha$ can be calculated as the difference of the total number of atoms in the cluster and the number of solutions for $E \neq \alpha$. This degeneracy $2(\lambda\mu + \lambda\nu + \mu\nu) +$

$+ \lambda + \mu + \nu + 1$ is equal to the difference of the number of atoms in the sublattices ○ and ●.

If $E = \alpha$, equations (3a) and (3b) become mutually independent,

$$\overset{\circ}{c}_{l-1,m-1,n-1} + \overset{\circ}{c}_{l-1,m+1,n+1} + \overset{\circ}{c}_{l+1,m-1,n+1} + \overset{\circ}{c}_{l+1,m+1,n-1} = 0\,, \tag{12a}$$

$$\overset{\bullet}{c}_{l+1,m+1,n+1} + \overset{\bullet}{c}_{l+1,m-1,n-1} + \overset{\bullet}{c}_{l-1,m+1,n-1} + \overset{\bullet}{c}_{l-1,m-1,n+1} = 0\,. \tag{12b}$$

It can easily be shown that (12b) together with boundary condition (4) has only the trivial solution $\overset{\bullet}{c}_{lmn} = 0$. On the other hand, the solution of (12a) is, despite of its simplicity, much more complicated. We do not give the detailed discussion of (12a) here and show that the knowledge of the explicit form of the solutions of (12a) is not necessary.

More exactly, we show that the Green function

$$G(E) = \sum_j \frac{|j\rangle\langle j|}{E - E_j + i\varepsilon}\,, \tag{13}$$

where $\sum_j$ denotes the summation over all states, does not depend on a particular form of the eigenvectors for $E = \alpha$ and can be calculated without the knowledge of these eigenvectors. The summation in (13) can be written as the summation over the energies $E_j < \alpha$, $E_j = \alpha$, and $E_j > \alpha$,

$$G(E) = \sum_j^{E_j<\alpha} \frac{|j\rangle\langle j|}{E - E_j + i\varepsilon} + \sum_j^{E_j=\alpha} \frac{|j\rangle\langle j|}{E - E_j + i\varepsilon} + \sum_j^{E_j>\alpha} \frac{|j\rangle\langle j|}{E - E_j + i\varepsilon}\,.$$

The second sum is due to the relation

$$\sum_j |j\rangle\langle j| = 1$$

equal to

$$\frac{1}{E - \alpha + i\varepsilon} \sum_j^{E_j=\alpha} |j\rangle\langle j| = \frac{1}{E - \alpha + i\varepsilon} \Big(1 - \sum_j^{E_j<\alpha} |j\rangle\langle j| - \sum_j^{E_j>\alpha} |j\rangle\langle j|\Big)\,.$$

Thus, any physical quantity which can be calculated by using the Green function can be found without the knowledge of the eigenvectors corresponding to $E = \alpha$.

## 6. Infinite Crystal Limit

For $L, M, N \to \infty$, formula (6) becomes the dispersion relation $E = E(\boldsymbol{k})$ of the infinite crystal (compare with (12) in [1]). Because of the absence of the surface, the sinusoidal and cosinusoidal form of eigenvectors (10) and (11), respectively, can be then replaced by the exponential form

$$\overset{\circ}{c}_{lmn}, \overset{\bullet}{c}_{lmn} \sim \mathrm{e}^{i\boldsymbol{k}\boldsymbol{r}_{lmn}}\,, \tag{14}$$

in agreement with the tight-binding method for the infinite crystal (see (1) and (2) in [1]). As the wave functions (14) corresponding to $\boldsymbol{k}$ and $-\boldsymbol{k}$ are linearly independent, the usual Brillouin zone of the infinite crystal instead of its part in the octant $k_x$, $k_y$, $k_z > 0$ (see Fig. 2) must be considered. The total number of the eigenvalues of the cluster in the form of the cube increases as $N^3$, in contrast to the degeneracy of the level $E = \alpha$ which increases as $N^2$. It means that with increasing $N$ the relative weight of the level $E = \alpha$ goes down and the corresponding peak in the density of states disappears for the infinite crystal.

## 7. Conclusions

The analytic solution of the tight-binding s-states model of the diamond clusters in the form of rectangular parallelepipeds has been found. In agreement with the experience from the infinite crystal calculations [1], we expect that our model describes well the states corresponding to the lowest part of the valence band of the diamond clusters (C, Si, and Ge). The extension of the results given here to the zincblende crystals (GaAs, ZnSe) is straightforward.

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